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Surfactants Based on Animal Fats

Agricultural Research Service
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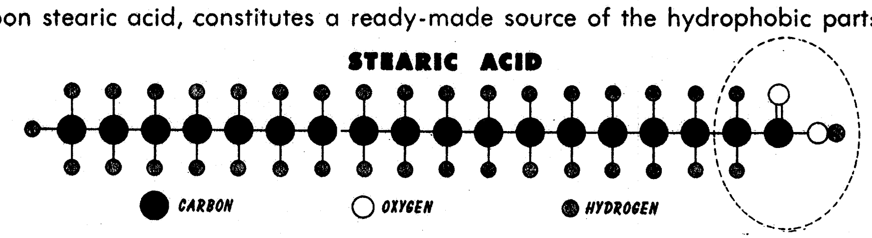
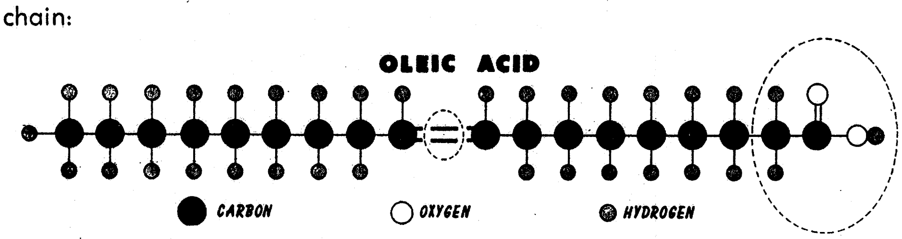
ANIMAL FATS: A MADE-TO-ORDER CHEMICAL RAW MATERIAL

The Eastern Utilization Research and Development Division (EURDD) of USDA's Agricultural Research Service has long been engaged in research on animal fats designed to maintain existing markets and to develop new uses. One line of this research concerns development of new and improved detergents and surface-active agents from animal fats. In many ways the fatty acids of meat fat are structurally ideal for carrying out reactions to produce biodegradable surfactants. Detergent molecules contain a hydrophobic part that is compatible with oil or grease and a hydrophilic part that attaches or orients itself toward water. The long paraffinic chain of tallow fatty acids, as for example 18-carbon stearic acid, constitutes a ready-made source of the hydrophobic part:



This paraffinic chain has a carboxyl group and alpha-hydrogen atoms to permit reactions that will introduce hydrophylic groups.

Oleic, the 18-carbon unsaturated acid from tallow, has a double bond at the center of the chain:



Derivatives of this unsaturated acid have greater water solubility than found in corresponding saturated derivatives of stearic acid and the 16-carbon palmitic acid. The double bond also permits addition reactions leading to products of enhanced hydrophilic properties. The completely straight-chain character of the fatty acids predisposes fat-based surfactants to ease of biodegradation.

FAT-BASED SURFACTANTS HAVE OUTSTANDING PROPERTIES

They Make Excellent Wetting Agents

Pelargonic acid, a derivative of oleic acid, yields a number of compounds that have exceptional wetting power. This is particularly true of the 2-ethylhexyl, capryl, and octyl esters of the sodium salt of alpha-sulfopelargonic acid. The wetting powers of dilute solutions of one of the most effective commercial wetting agents and an experimentally developed pelargonic acid derivative, with water as control, are compared in figure 1.

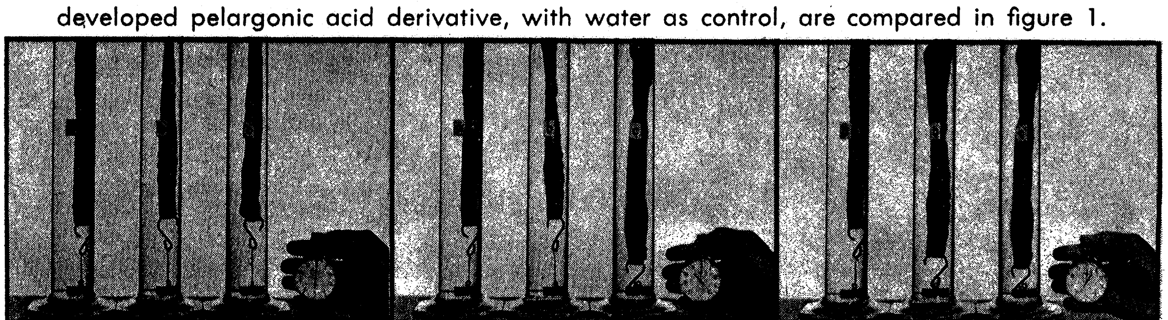


Figure 1. Comparative wetting of weighted cotton skeins (a) in water (control), (b) in 0.05 percent solution of a commercial wetting agent (dioctyl sodium sulfosuccinate), and (c) in 0.05 percent solution of an experimental fat-based surfactant (2-ethylhexyl ester of sodium alpha-sulfopelargonate). Fat-based compound causes skein to sink in 3.7 seconds, commercial wetting agent in 5.7 seconds. In the absence of any wetting agent, skein does not sink for 4 hours.

The alpha-sulfopelargonates have an additional advantage as wetting agents in their stability against hydrolysis in alkaline or acid solutions. This is important in such applications as textile dyeing.

Pelargonic acid is obtainable along with azelaic acid in the splitting of oleic acid in the presence of ozone:

$$\underset{\text{Oleic acid}}{H_3C\text{-}(CH_2)_7\text{-}\overset{H}{\underset{|}{C}}{=}\overset{H}{\underset{|}{C}} - (CH_2)_7\text{-}COOH} \xrightarrow{+O_3} \begin{array}{c} H_3C\text{-}(CH_2)_7\text{-}COOH \\ \text{Pelargonic acid} \\ \text{and} \\ HOOC\text{-}(CH_2)_7\text{-}COOH \\ \text{Azelaic acid} \end{array}$$

Azelaic acid has been used for years in the production of plasticizers and lubricants. It has a promising future in the preparation and modification of high-molecular-weight polymers. It can serve well as the dibasic acid in preparing nylons, polyesters, and polyurethanes. Azelaic acid would be expected to be cheaper if one or more major uses could be developed for pelargonic acid. (Azelaic acid 36-37 cents per pound and pelargonic acid 26 to 29½ cents per pound, large quantities, delivered to New York City, July 28, 1967.) Thus, the interrelated pelargonic and azelaic acids from animal fat seem to offer an attractive commercial opportunity.

They Combine with Synergistic Advantage

The alpha-sulfo esters and the tallow alcohol sulfates as separate groups have desirable surface-active properties. When they are combined, the properties of these two groups of surfactants are enhanced more than would be accounted for by additive effects. Determinations of hard-water solubility, wetting power, foam production, and detergency have been used to compare different types of surfactants individually and in combinations. The combination of saturated or unsaturated tallow alcohol sulfate with the methyl ester of the sodium salt of alpha-sulfo saturated tallow fatty acid appears outstanding.

Tallow soap takes on new surface-active properties in hard water when tallow alcohol sulfates or alpha-sulfo tallow fatty acid derivatives are added to it. Research at EURDD has also shown that the addition of one of the more soluble tallow alcohol sulfates improves the performance of liquid detergent formulations containing soap and an alpha-sulfo derivative. Thus, sodium 9,10-dichlorooctadecyl sulfate exerts a synergistic effect in combination with sodium oleate and disodium 2-sulfoethyl alpha-sulfostearate.

The synergistic effect of the built surfactant mixtures (0.05 percent total active ingredient plus 0.20 percent builder) can be illustrated quantitatively in a particular experiment in which standard soiled cotton was washed in hard water (300 p.p.m. $CaCO_3$) at 60° C. The value for increase in reflectance ($\triangle$ R) after washing was 31.7 for sodium methyl alpha-sulfotallowate and 30.7 for the sodium salt of unsaturated tallow alcohol sulfate. Binary mixtures of the two had $\triangle$ R values in the range of 32.8 to 34.2, greater in all ratios than the $\triangle$ R value for the more active component alone.

Detergent formulators for many years have used certain combinations of surface-active agents to obtain synergistic effects. The examples cited above merely illustrate some of those found in our research. Undoubtedly many other favorable combinations employing tallow alcohol sulfates and alpha-sulfo esters remain to be discovered.

They Make Excellent Detergents in Hard Water

Detergents made from tallow are, in general, superior to branched-chain alkylbenzenesulfonate (ABS) and linear alkylbenzenesulfonate (LAS) in hard as well as soft water. Table 1 shows the result of a typical test in which detergency values of two fat-based

TABLE 1.—Detergency of tallow derivatives and petroleum-based products.
(Basis: 0.25 percent soap solution in soft water = 100)

0.25 percent built detergents[1]	*Detergency value* Soft water	Hard water[2]
Tallow alcohol sulfate[3]	101	98
Alpha-sulfo tallow ester[4]	92	91
Tallow ester-soap mixture, 1:1[5]	99	89
ABS	86	76
LAS	86	85

1 0.05 percent active ingredient plus 0.20 percent inorganic builder.

2 300 p.p.m. of $CaCO_3$.

3 Na tetradecyl sulfate, 6 percent; Na hexadecyl sulfate, 28 percent; Na octadecyl sulfate, 66 percent.

4 Me esters of Na alpha-sulfomyristate, 6 percent; Na alpha-sulfopalmitate, 28 percent; Na alpha-sulfostearate, 66 percent.

5 A mixture of alpha-sulfo tallow ester and commercial tallow-soap flakes.

detergents, tallow alcohol sulfate and alpha-sulfo tallow ester, and a 1:1 mixture of ester and commercial soap flakes are compared with ABS and LAS. The figures show the tallow alcohol sulfate about equivalent in detergency to soap in soft water. The tallow alcohol sulfate was about as good in hard water as in soft water. The alpha-sulfo ester, although slightly inferior in soft water, performed almost as well as the tallow alcohol sulfate in hard water. The poorest of the three tallow formulations in hard water was the ester-soap mixture, but even this was superior to ABS and comparable to LAS.

They Are Readily Biodegradable

The tallow alcohol sulfates are superior to LAS, as well as ABS, in completeness and speed of biodegradation in river and surface waters and in sewage systems.

In the river water die-away test (using methylene blue analysis to determine undegraded detergent), tallow alcohol sulfate practically disappeared in 1 day, from an initial concentration of 5 p.p.m., as shown in figure 2. The LAS degraded in 5 days, while the ABS persisted for 30 days.

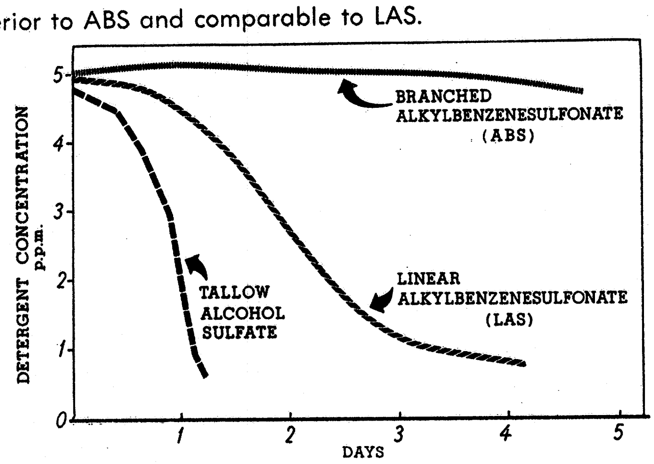


Figure 2. Biodegradability of detergents as measured in river water die-away test.

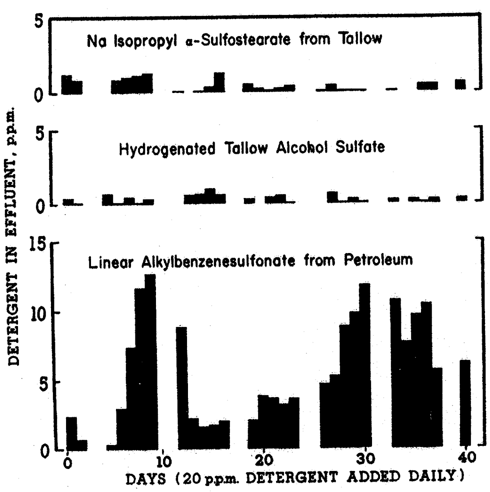


Figure 3. Breakdown of fat-based detergents and LAS in an activated sludge system.

In an activated sludge system simulating a sewage plant, tallow alcohol sulfate and alpha-sulfo tallow ester are both far superior to LAS in ease of breakdown, as figure 3 shows. This bar chart presents the results of experiments in which 20 p.p.m. of detergent was added daily to such a system for 40 days. Daily checks showed that when the detergent was either one of the fat derivatives the concentration of undegraded detergent remaining in the effluent rarely rose above 1 p.p.m. By contrast, the LAS concentration rose rapidly after the first few days and remained between 3 and 13 p.p.m. for the length of the experiment.

The relative ease of biodegradation of fat-based detergents is particularly important under anaerobic conditions. About a third of the private dwellings in the United States have anaerobic septic tanks, and on-site wells provide the water supply for some of these dwellings.[1] In certain instances household wastes, including detergents and other soluble organic materials, may have insufficient opportunity to degrade before reaching the water table and thus the well water. Not only do many householders have a direct interest in detergents of maximum anaerobic biodegradability, but industrialists are also concerned about situations in which processing wastes receive insufficient aeration.

Experiments have been performed on the anaerobic digestion of eight anionic detergents, including alcohol sulfates, alpha-sulfo fatty acid esters, and LAS. In these experiments gas production (methane) was taken as a measure of effective sludge digestion, and the residual detergent concentration in the effluent was followed as a check on the degradation. In this anaerobic system the tallow alcohol sulfates readily and completely degraded. The LAS not only failed to degrade, but it disrupted the normal anaerobic digestion, almost cutting off gas evolution. The alpha-sulfo esters did not degrade either, but they had no adverse effect on the bacteriological digestion. True, in these tests the concentration of detergent was higher than it would become under normal conditions of anaerobic digestion. But the fat-based compounds have an obvious advantage in that even at high concentrations they do not destroy the very microorganisms that must be depended upon to digest them.

[1] Chemical and Engineering News, **45** (9): 20. Feb. 27, 1967.

In lysimeter studies in which the detergent solutions were allowed to percolate through stone chips and soil, the following results were obtained upon examining the effluent: 100 percent degradation of sodium isopropyl alpha-sulfostearate, 83 percent degradation of LAS, and 35 percent degradation of ABS.

ANIMAL FATS ARE ABUNDANT, RECURRING, AND INEXPENSIVE

Tremendous quantities of animal fats are made available each year for industrial exploitation as byproducts of the American livestock industry. As the population grows in numbers and affluence, the demand for meat increases, thus ensuring an abundant supply of fats. Beyond the lard and edible tallow that go into shortenings and other food products, these fats are processed as inedible grades and are far in excess of the present domestic demand in industrial uses. In 1966 more than 2 billion pounds of tallow was exported, nearly one-half the total production of inedible fats.

While the quantity of animal fat used in soap dropped sharply in the last 20 years, overall nonfood usage has actually increased. Addition of fat to feeds, production of fatty acids, and miscellaneous industrial outlets have accounted for this. The supply of animal fats, however, is sufficiently large and constant to ensure that a reasonable price prevails. During the period 1962-66, the average annual production of inedible tallow was 4.3 billion pounds. The average price for inedible tallow No. 1 at Chicago for this period was 5.8 cents per pound (range: 4.5 to 7.2 cents). Thus manufacturers of surface-active agents are offered an abundant raw material that is inexpensive and not subject to inordinate price fluctuation.

SURFACTANTS CAN BE READILY PRODUCED FROM FATS AND FATTY ACIDS

Tallow and other animal fats make up the raw materials from which stearic, palmitic, and oleic acids are derived by hydrolysis. The tallow alcohols, of course, are produced by reducing the acids back to the corresponding alcohols. Other derivatives of fatty acids, such as amides and nitriles, may also be considered as raw materials for synthesis.

Alpha-sulfonation with sulfur trioxide is a specific, inexpensive reaction easily carried out with saturated fatty acids but not so with unsaturated. Recent work at the EURDD Laboratory has shown it is possible to alpha-sulfonate saturated esters directly with sulfur trioxide. This may make it possible to avoid using a reaction solvent and also permit other advantages. Industrial producers of sulfur trioxide and of sulfonation equipment can provide information on carrying out large-scale sulfonation reactions.

Sulfation of fatty alcohols has been practiced for many years commercially. It may be carried out with a variety of sulfating agents including sulfuric acid, chlorosulfonic acid, sulfur trioxide, dioxane-sulfur trioxide, and sulfamic acid.

While only a few of the surfactants derivable from animal fats are mentioned here, a large number have been prepared at the Eastern Regional Research Laboratory. Likewise, many reactions are being carried out on tallow fatty acids or tallow alcohols to increase the aqueous solubility of the surfactant derivatives. Such reactions include catalytic hydrogenolysis of fat to produce alcohols without hydrogenation at the double bond; additive chlorination; preparation of triethanolammonium salts of alpha-sulfonated fatty acids; and oxyalkylation and sulfation of saturated tallow alcohols.

Preliminary evaluation of relative toxicity and skin tests were made on alpha-sulfo and alpha-phosphono compounds of types discussed in this brochure. The tests indicate that these compounds are relatively safe and free of irritation.

SELECTED PUBLICATIONS AND PATENTS

Reprints of these publications are available on request from the Eastern Utilization Research and Development Division, 600 East Mermaid Lane, Philadelphia, Pa. 19118. Please request by EU publication number.

alpha-Sulfonation

1. Weil, J. K., L. P. Witnauer, and A. J. Stirton. EVIDENCE FOR ALPHA-SULFONATION IN THE REACTION OF PALMITIC ACID WITH SULFUR TRIOXIDE. J. Amer. Chem. Soc., **75:** 2526-2527. 1953. (EU pub. No. 766.)
2. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton. SYNTHETIC DETERGENTS FROM ANIMAL FATS. IX. TRIETHANOLAMMONIUM, LITHIUM, ALKALINE EARTH, AND OTHER SALTS OF ALPHA-SULFONATED FATTY ACIDS. J. Amer. Oil Chemists' Soc., **34:** 100-103. 1957. (EU pub. No. 1117.)
3. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and W. C. Ault. THE ALPHA-SULFONATION OF PELARGONIC, STEARIC AND SUBSTITUTED STEARIC ACIDS. J. Amer. Oil Chemists' Soc., **37** (12): 679-682. 1960. (EU pub. No. 1531.)
4. Stirton, A. J. ALPHA-SULFO FATTY ACIDS AND DERIVATIVES, SYNTHESIS, PROPERTIES AND USE. J. Amer. Oil Chemists' Soc., **39** (11): 490-496. 1962. (EU pub. No. 1848.)

alpha-Sulfo Esters

Wetting Agents, Detergents, and Lime Soap Dispersing Agents

5. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton. SODIUM SALTS OF ALKYL ALPHA-SULFOPALMITATES AND STEARATES. J. Amer. Chem. Soc., **75:** 4859-4860. 1953. (EU pub. No. 805.)
6. Stirton, A. J., J. K. Weil, and R. G. Bistline, Jr. SURFACE-ACTIVE PROPERTIES OF SALTS OF ALPHA-SULFONATED ACIDS AND ESTERS. J. Amer. Oil Chemists' Soc., **31:** 13-16. 1954. (EU pub. No. 847.)
7. Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton. SYNTHETIC DETERGENTS FROM ANIMAL FATS. V. ESTERS FROM ALPHA-SULFONATED FATTY ACIDS AND SODIUM ISETHIONATE. J. Amer. Oil Chemists' Soc., **32:** 370-372. 1955. (EU pub. No. 929.)
8. Bistline, R. G., A. J. Stirton, J. K. Weil, and W. S. Port. SYNTHETIC DETERGENTS FROM ANIMAL FATS. VI. POLYMERIZABLE ESTERS OF ALPHA-SULFONATED FATTY ACIDS. J. Amer. Oil Chemists' Soc., **33:** 44-45. 1956. (EU pub. No. 982.)
9. Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, and W. C. Ault. SODIUM ALKYL ALPHA-SULFOPELARGONATES $C_7H_{15}CH(SO_3Na)CO_2R$. WETTING AND RELATED PROPERTIES. J. Amer. Oil Chemists' Soc., **39** (1): 55-58. 1962. (EU pub. No. 1701.)
10. Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, W. C. Ault, and E. W. Maurer. SODIUM SALTS OF ALKYL ESTERS OF ALPHA-SULFO FATTY ACIDS, WETTING, LIME SOAP DISPERSION, AND RELATED PROPERTIES. J. Amer. Oil Chemists' Soc., **39:** 128-131. 1962. (EU pub. No. 1714.)
11. Stirton, A. J., R. G. Bistline, Jr., E. A. Barr, and M. V. Nunez-Ponzoa. SALTS OF ALKYL ESTERS OF ALPHA-SULFOPALMITIC AND ALPHA-SULFOSTEARIC ACIDS. J. Amer. Oil Chemists' Soc., **42** (12): 1078-1081. 1965. (EU pub. No. 2355.)

Tallow Alcohol Sulfates

12. Weil, J. K., A. J. Stirton, R. G. Bistline, Jr., and E. W. Maurer. TALLOW ALCOHOL SULFATES, PROPERTIES IN RELATION TO CHEMICAL MODIFICATION. J. Amer. Oil Chemists' Soc., **36** (6): 241-244. 1959. (EU pub. No. 1333.)

Nonionics

13. Wrigley, A. N., F. D. Smith, and A. J. Stirton. SYNTHETIC DETERGENTS FROM ANIMAL FATS. VIII. THE ETHENOXYLATION OF FATTY ACIDS AND ALCOHOLS. J. Amer. Oil Chemists' Soc., **34:** 39-43. 1957. (EU pub. No. 1124.)

Biodegradation

14. Weil, J. K., and A. J. Stirton. BIODEGRADATION OF SOME TALLOW-BASED SURFACE ACTIVE AGENTS IN RIVER WATER. J. Amer. Oil Chemists' Soc., **41** (5): 355-358. 1964. (EU pub. No. 2058.)
15. Cordon, T. C., E. W. Maurer, J. K. Weil, and A. J. Stirton. BIODEGRADATION OF ESTERS OF ALPHA-SULFO FATTY ACIDS IN ACTIVATED SLUDGE. Developments in Industrial Microbiology, **6:** 3-15. 1964. (EU pub. No. 2181.)
16. Maurer, E. W., T. C. Cordon, J. K. Weil, M. V. Nunez-Ponzoa, W. C. Ault, and A. J. Stirton. THE EFFECT OF TALLOW-BASED DETERGENTS ON ANAEROBIC DIGESTION. J. Amer. Oil Chemists' Soc., **42** (3): 189-192. 1965. (EU pub. No. 2219.)

Formulations

17. Stirton, A. J., E. W. Maurer, and J. K. Weil. SYNTHETIC DETERGENTS FROM ANIMAL FATS. VII. DETERGENT COMBINATIONS. J. Amer. Oil Chemists' Soc., **33:** 290-291. 1956. (EU pub. No. 1014.)
18. Bistline, R. G., Jr., and A. J. Stirton. EXPERIMENTS IN THE FORMULATION OF HEAVY DUTY LIQUID DETERGENTS FROM TALLOW. J. Amer. Oil Chemists' Soc., **41** (10): 654-656. 1964. (EU pub. No. 2132.)
19. Stirton, A. J., R. G. Bistline, Jr., Eileen B. Leardi, and M. V. Nunez-Ponzoa. TALLOW-BASED DETERGENT FORMULATIONS: MIXTURES OF ALCOHOL SULFATES, SALTS OF ALPHA-SULFO ACIDS AND ESTERS, AND SOAP. J. Amer. Oil Chemists' Soc., **44** (2): 99-102. 1967. (EU pub. No. 2562.)

Amides; Detergent Bars

20. Weil, J. K., A. J. Stirton, and R. G. Bistline, Jr. AMIDES OF ALPHA-SULFONATED PALMITIC AND STEARIC ACIDS. J. Amer. Oil Chemists' Soc., **37** (6): 295-297. 1960. (EU pub. No. 1456.)
21. Weil, J. K., A. J. Stirton, E. W. Maurer, W. C. Ault, and W. E. Palm. DETERGENT BARS FROM SALTS OF ALPHA-SULFONATED TALLOW ACIDS. J. Amer. Oil Chemists' Soc., **35** (9): 461-465. 1958. (EU pub. No. 1264.)

Diesters and Diamides

22. Weil, J. K., A. J. Stirton, and R. G. Bistline, Jr. DIESTERS AND DIAMIDES OF ALPHA-SULFOPALMITIC AND ALPHA-SULFOSTEARIC ACIDS. J. Amer. Oil Chemists' Soc., **39:** 168-170. 1962. (EU pub. No. 1727.)

Decarboxylation

23. Weil, J. K., F. D. Smith, and A. J. Stirton. ALKANESULFONATES AND HYDROXYALKANESULFONATES FROM ALPHA-SULFO FATTY ACIDS. J. Organ. Chem. **27:** 2950-2952. 1962. (EU pub. No. 1791.)

Critical Micelle Concentration

24. Weil, J. K., and A. J. Stirton. CRITICAL MICELLE CONCENTRATIONS OF ALPHA-SULFONATED FATTY ACIDS AND THEIR ESTERS. J. Phys. Chem., **60:** 899-901. 1956. (EU pub. No. 1067.)

PATENTS

2,806,044 Weil, J. K., R. G. Bistline, Jr., and A. J. Stirton. **ESTERS OF HYDROXYALKANESULFONATES WITH ALPHA-SULFONATED LONG CHAIN FATTY ACIDS. Issued September 10, 1957.**

2,844,606 Bistline, R. G., Jr., W. S. Port, A. J. Stirton, and J. K. Weil. **POLYMERIZABLE ESTERS OF ALPHA-SULFONATED FATTY ACIDS. Issued July 22, 1958.**

3,128,294 Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, and W. C. Ault. **SALTS OF ALPHA-SULFONATED FATTY ACID ESTERS. Issued April 7, 1964.**

3,219,584 Stirton, A. J., R. G. Bistline, Jr., J. K. Weil, and W. C. Ault. **WETTING AGENTS AND SURFACE ACTIVE COMPOSITIONS THEREFROM. Issued November 23, 1965.**

2,915,473 Stirton, A. J., J. K. Weil, and E. W. Maurer. **DETERGENT COMPOSITIONS. Issued December 1, 1959.**

2,867,586 Weil, J. K., A. J. Stirton, and E. W. Maurer. **SYNTHETIC DETERGENT BAR COMPOSITIONS. Issued January 6, 1959.**

To obtain a license to practice under an assigned patent, send a letter of application to the Administrator, Agricultural Research Service, U.S. Department of Agriculture, Washington, D.C. 20250. The letter should give the title and patent number of the invention, and the name and principal place of business of the proposed licensee, together with the name of the person who is authorized to sign on behalf of the licensee. The Department will prepare the necessary form of license for execution.

It is suggested that any individual or organization intending to manufacture the surface-active agents covered in this brochure first investigate the patent situation. We cannot guarantee the absence of non-government patents that may cover some aspects of the production or use of some of the compounds mentioned.